



**VERIFICATION OF TRANSLATION**

I, Shigeki Nakatsukasa declare as follows:

1. That I am well acquainted with both the English and Japanese languages, and
2. that the attached document is a true and correct translation made by me to the best of my knowledge and belief of the following Japanese patent application:

**Japanese Patent Application No. JP2001-011051 filed January 19, 2001.**

3. The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

July 5, 2004  
Date

Shigeki Nakatsukasa  
Print Name of Translator

S. Nakatsukasa  
Signature of Translator



**JAPAN PATENT OFFICE**

This is to certify that the annexed is a true copy of the following application as filed with this Office.

Date of Application : January 19, 2001

Application Number : Japanese Patent Application  
No. 2001-011051

Applicant(s) : Kuraray Co., Ltd.

October 19, 2001

Commissioner,

Japan Patent Office: Kozo Oikawa (Seal)

Issuance No. 2001-3092611

[Document Name] Patent Application  
[Reference Number] K00780AP00  
[Filing Date] January 19, 2001  
[Addressee] Commissioner of Patent Office  
[International Patent Classification] C08F216/06  
[Inventor]

[Address or Residence]

c/o Kuraray Co., Ltd.

1-2-1, Kaigan-dori, Okayama-City, Okayama-Pref.

[Name] Takaharu Kawahara

[Inventor]

[Address or Residence]

c/o Kuraray Co., Ltd.

1-2-1, Kaigan-dori, Okayama-City, Okayama-Pref.

[Name] Toshio Tuboi

[Inventor]

[Address or Residence]

c/o Kuraray Co., Ltd.

1-2-1, Kaigan-dori, Okayama-City, Okayama-Pref.

[Name] Yukihiro Ohara

[Inventor]

[Address or Residence]

c/o Kuraray Co., Ltd.

1621, Sakazu, Kurashiki-City, Okayama-Pref.

[Name] Masao Hikasa

**[Inventor]****[Address or Residence]**

c/o Kuraray Co., Ltd.

1621, Sakazu, Kurashiki-City, Okayama-Pref.

**[Name]** Hiroshi Kawai**[Applicant]****[Identification Number]** 000001085**[Name or Title]** Kuraray Co., Ltd.**[Representative]** Yasuaki Wakui**[Phone Number]** 03-3277-3182**[Indication of Fees]****[Prepayment Book Number]** 008198**[Amount of Payment]** 21,000 yen**[List of Submitted Article]****[Article Name]** Specification 1 copy**[Article Name]** Drawing 1 copy**[Article Name]** Abstract 1 copy**[Request for proof]** Yes

[Designation of Document]      Specification

[Title of the Invention]

METHOD FOR PRODUCING ETHYLENE-VINYL ALCOHOL COPOLYMER RESIN

[Claims]

[Claim 1]    A method for producing an ethylene-vinyl alcohol copolymer resin, which comprises

    a step of introducing an ethylene-vinyl alcohol copolymer solution that contains at least 50 parts by weight, relative to 100 parts by weight of the ethylene-vinyl alcohol copolymer therein, of an alcohol having a boiling point of not higher than 100°C, into an apparatus, and contacting it with water in the apparatus, thereby letting the alcohol out along with water and taking the resulting aqueous ethylene-vinyl alcohol copolymer composition that contains from 0 to 10 parts by weight of the alcohol and from 10 to 1000 parts by weight of water, relative to 100 parts by weight of the ethylene-vinyl alcohol copolymer therein, out of the apparatus (step 1), and

    a step of feeding the aqueous ethylene-vinyl alcohol copolymer composition into an extruder, kneading it in melt therein, and then extruding the copolymer out of the extruder (step 2).

[Claim 2]    The method for producing an ethylene-vinyl alcohol copolymer resin as claimed in claim 1, wherein the ethylene content of the ethylene-vinyl alcohol copolymer falls between 3 and 70 mol% and the degree of saponification thereof is at

least 80 mol%.

[Claim 3] The method for producing an ethylene-vinyl alcohol copolymer resin as claimed in claim 1 or 2, wherein the alcohol is methanol.

[Claim 4] The method for producing an ethylene-vinyl alcohol copolymer resin as claimed in any of claims 1 to 3, wherein in the step 1, the ethylene-vinyl alcohol copolymer solution is introduced into a vessel and contacted with water vapor in the vessel, thereby letting the alcohol out along with water vapor and taking the resulting aqueous ethylene-vinyl alcohol copolymer composition out of the vessel.

[Claim 5] The method for producing an ethylene-vinyl alcohol copolymer resin as claimed in claim 4, wherein the ethylene-vinyl alcohol copolymer solution is continuously introduced into a column vessel and contacted with water vapor in the vessel.

[Claim 6] The method for producing an ethylene-vinyl alcohol copolymer resin as claimed in claim 5, wherein the ethylene-vinyl alcohol copolymer solution is introduced into the vessel through its upper part with water vapor through its lower part to thereby make the ethylene-vinyl alcohol copolymer solution contacted with water vapor in countercurrent flow, and the resulting aqueous ethylene-vinyl alcohol copolymer composition is taken out of the vessel through its lower part with the alcohol being let out through its upper part along with water vapor.

[Claim 7] The method for producing an ethylene-vinyl alcohol

copolymer resin as claimed in any of claims 1 to 6, wherein in the step 2, the temperature of the resin melt in the extruder falls between 70 and 170°C.

[Claim 8] The method for producing an ethylene-vinyl alcohol copolymer resin as claimed in any of claims 1 to 7, wherein in the step 2, the water content of the resin melt just extruded out of the extruder falls between 5 and 40 % by weight.

[Claim 9] The method for producing an ethylene-vinyl alcohol copolymer resin as claimed in any of claims 1 to 8, wherein in the step 2, necessary water is fed into the extruder or excess water is removed from it to thereby control the water content of the resin in the extruder.

[Claim 10] The method for producing an ethylene-vinyl alcohol copolymer resin as claimed in any of claims 1 to 9, wherein in the step 2, the aqueous ethylene-vinyl alcohol copolymer composition is kneaded in melt in the extruder with at least one additive selected from carboxylic acids, boron compounds, phosphoric acid compounds, alkali metal salts and alkaline earth metal salts fed thereinto.

[Claim 11] The method for producing an ethylene-vinyl alcohol copolymer resin as claimed in claim 10, wherein an aqueous solution of the additive is fed into the extruder.

[Claim 12] The method for producing an ethylene-vinyl alcohol copolymer resin as claimed in any of claims 1 to 11, wherein in the step 2, a wash is fed into the extruder and it is discharged

from it through at least one site downstream the wash inlet site to thereby remove the saponification catalyst residue from the resin melt.

- [Claim 13] The method for producing an ethylene-vinyl alcohol copolymer resin as claimed in any of claims 1 to 12, wherein the aqueous ethylene-vinyl alcohol copolymer composition taken out of the apparatus in the step 1 is cut into pellets, and the resulting pellets are fed into the extruder in the step 2.

[Claim 14] The method for producing an ethylene-vinyl alcohol copolymer resin as claimed in claim 13, wherein the pellets are dipped in a wash to remove the saponification catalyst residue from them, and then fed into the extruder in the step 2.

[Claim 15] The method for producing an ethylene-vinyl alcohol copolymer resin as claimed in claim 14, wherein the pellets are continuously washed in a column vessel.

[Claim 16] The method for producing an ethylene-vinyl alcohol copolymer resin as claimed in any of claims 13 to 15, wherein the pellets are dipped in an aqueous solution containing at least one additive selected from carboxylic acids, boron compounds, phosphoric acid compounds, alkali metal salts and alkaline earth metal salts to thereby add the additive to the pellets, and then they are fed into the extruder in the step 2.

[Claim 17] The method for producing an ethylene-vinyl alcohol copolymer resin as claimed in any of claims 1 to 12, wherein the aqueous ethylene-vinyl alcohol copolymer composition taken



out of the apparatus in melt in the step 1 is, not cut, fed into the extruder in the step 2.

[Claim 18] The method for producing an ethylene-vinyl alcohol copolymer resin as claimed in claim 17, wherein the aqueous ethylene-vinyl alcohol copolymer composition is, not cut, fed into the extruder in the step 2, and a wash is fed into the extruder and discharged from it through at least one site downstream the wash inlet site to thereby remove the saponification catalyst residue from the resin melt.

[Claim 19] A method for producing ethylene-vinyl alcohol copolymer resin pellets, which comprises cutting the ethylene-vinyl alcohol copolymer resin that is extruded out of the extruder in the step 2 in the method of any of claims 1 to 18.

[Claim 20] The method for producing ethylene-vinyl alcohol copolymer resin pellets as claimed in claim 19, wherein the pellets are, after cut, dried to have a water content of at most 1 % by weight.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Belongs]

The present invention relates to a method for producing an ethylene-vinyl alcohol copolymer (EVOH) resin, and to a method for producing EVOH resin pellets by cutting the EVOH resin produced according to the former method.

More precisely, the invention relates to a method for producing an EVOH resin, which comprises a step of introducing an alcohol-containing EVOH solution into an apparatus, and contacting it with water in the apparatus, thereby letting the alcohol out along with water and taking the resulting aqueous EVOH composition out of the apparatus, and a step of feeding the aqueous EVOH composition into an extruder, kneading it in melt therein, and then extruding it out of the extruder; and relates to a method for producing EVOH resin pellets by cutting the EVOH resin produced according to the former method.

Description of the Related Art:

[0002]

[Prior Art]

Ethylene-vinyl alcohol copolymer is a useful polymer material having good oxygen barrier properties, aroma retentiveness, oil resistance, antistatic properties and mechanical strength, and is widely used for films, sheets, containers, etc. One general method of producing EVOH comprises saponifying an ethylene-vinyl ester copolymer that is obtained through polymerization of ethylene with a vinyl ester of a fatty acid such as vinyl acetate or the like, in an alcohol-containing organic solvent in the presence of a saponification catalyst.

[0003]

For post-treating the alcohol solution of EVOH obtained through saponification, for example, Japanese Patent

Publication No. 38634/1972 discloses a method of producing EVOH pellets which comprises adding water to an optionally-concentrated methanol solution of EVOH to such a degree that no EVOH deposit is formed therein to prepare a methanol-water mixed solution of EVOH that contains from 15 to 45 % by weight of EVOH, then extruding it into strands in water or in a methanol-water mixed solution having a lower methanol concentration than the EVOH solution, at 50°C or lower, and thereafter cutting the strands. They say that the methanol concentration in the methanol-water mixed solution in the coagulating bath preferably falls between 10 and 50 % by weight. They further say that the pellets thus obtained are porous and can be readily washed with water to remove the saponification catalyst residue and that the pellets are easy to handle in the subsequent washing and drying step.

[0004]

Regarding the process of adding water to a methanol solution of the EVOH after saponification, for example, demonstrated in Example 1 of Japanese Patent Laid-Open No. 90927/1999 is a method of producing a completely transparent, uniform methanol/water solution of EVOH, which comprises adding an aqueous methanol solution having a water content of 62.5 % by weight to a methanol solution of EVOH having an EVOH content of 30 % by weight, under an azeotropic condition at 100 °C to 110°C under a pressure of 3 kg/cm<sup>2</sup>G so as to remove methanol

until the EVOH content of the resulting EVOH solution increases up to 40 % by weight.

[0005]

However, in the method of producing EVOH pellets by coagulating an EVOH solution that contains a large amount of methanol, the alcohol often vaporizes in the step of coagulation. The alcohol vapor worsens the working environment and injures the health of the workers, and, in addition, it has negative influences on the area around the working site. Therefore, improving the method is desired.

[0006]

In case where EVOH having an ethylene content of smaller than 20 mol% or a degree of saponification of smaller than 95 % is produced according to the method as above, EVOH strands are difficult to form in the coagulating bath since the coagulation rate of EVOH in the bath is low. As a result, the EVOH strands, even though formed, are often miscut and are often contaminated with fine powder. Anyhow, stable production of EVOH pellets in the method is difficult. Even EVOH having an ethylene content of 20 mol% or more and a degree of saponification of 95 % or more is poorly coagulated or is difficult to handle, when it is coagulated in strands at an increased coagulation rate through an increased number of nozzles so as to increase the production efficiency, and, as a result, its strands are often miscut and stable production of its pellets is not easy.

[0007]

In addition, the EVOH pellets obtained in the conventional methods contain alcohol and the catalyst residue in saponification, alkali metal salts, and therefore require washing to remove them. To increase the washing speed, elevating the temperature of the washing liquid will be effective. However, if the temperature is elevated too high, the pellets will fuse as they contain alcohol. Therefore, the problem is that the washing speed could not be increased so high.

[0008]

On the other hand, various methods are known for molding EVOH pellets into various moldings. In general, EVOH pellets are molded in melt in a mode of, for example, extrusion or injection molding for which are used extruders. To mold it in such a manner, the starting material of EVOH resin pellets is first fed into the hopper of an extruder. In general, however, the temperature of the resin melt to be molded in that manner must not be lower than 200°C, and EVOH containing no additive will be readily degraded while molded in melt in that condition, thereby often forming fish eyes or hard spots in the products to lower the quality of the products.

[0009]

To solve the problem, known is a method of adding minor components such as acid substances and/or metal salts to EVOH. For example, for improving the long-run workability of EVOH and

for preventing EVOH moldings from having surface defects such as typically gels or hard spots that worsen the outward appearance of the moldings, disclosed is an EVOH composition which contains from 0.0005 to 0.05 % by weight in terms of the metal of a metal salt of the Group 2 of the Periodic Table, from 0.002 to 0.2 % by weight of an acid having a pKa of at least 3.5 and a boiling point not lower than 180°C, and from 0.01 to 0.2 % by weight of an acid having pKa of at least 3.5 and a boiling point not higher than 120°C, and which has specific flow properties (Japanese Patent Laid-Open No. 66262/1989).

[0010]

The following are examples of the method for obtaining EVOH pellets containing minor components as above: (1) A method of spraying an aqueous solution of minor components on EVOH pellets followed by mixing them in a Henschel mixer and drying them (Japanese Patent Laid-Open No. 12108/1980). (2) A method of adding powdery minor components to EVOH pellets followed by blending them in dry in a super-mixer (Japanese Patent Laid-Open No. 34148/1982). (3) A method of dipping EVOH pellets in an aqueous solution of minor components followed by dewatering and drying them (Japanese Patent Laid-Open No. 66262/1989). (4) A method of controlling the water content of EVOH pellets to fall between 20 and 80 % by weight followed by contacting the thus-controlled EVOH pellets with an aqueous solution of at least one compound selected from boron compounds, acetates and

phosphoric acid compounds (WO99/05213).

[0011]

In the methods (1) and (2), however, the minor components added to the EVOH pellets could not be uniformly dispersed. In addition, the amount of the minor components to be added is difficult to control, and products of stable quality are difficult to obtain. On the other hand, the methods (3) and (4) are advantageous in that the content of the minor components to be in the EVOH pellets is easy to control by controlling the concentration of the solution of the minor components. However, the EVOH pellets processed in these methods are still problematic in that their melt extrusion increases the motor torque and torque change of the extruder used. To solve the problem, in general, a lubricant is added to the EVOH pellets that are molded through extrusion. The lubricant may be added to EVOH resin pellets for preventing them from blocking while they are fed into extruder. Anyhow, however, the lubricant is unfavorable to EVOH resins for applications to food wrapping or packaging from the viewpoint of sanitation and safety. It is therefore desired to reduce the lubricant in EVOH resins and even not to use it therein.

[0012]

As so mentioned hereinabove, pellets of EVOH having an ethylene content of smaller than 20 mol% and those having a degree of saponification of smaller than 95 % are difficult to stably produce, and, as the case may be, they often form crumbs. Even

though EVOH having an ethylene content of at least 20 mol% and EVOH having a degree of saponification of at least 95 % may often form crumbs when they are processed into strands at high speed through an increased number of nozzles for enhancing the production efficiency. However, when the crumbed EVOH is processed according to the method of (3) or (4), the minor components are difficult to uniformly mix with it, and, as a result, products of stable quality could not be obtained.

[0013]

From the viewpoint of the production process, the conventional method of dipping EVOH pellets in a treating solution that contains an acid substance and/or a metal salt is troublesome as it requires a treating bath or column for dipping the pellets therein. In the treating solution used in such a treating bath or column, the acidic substance and/or the metal salt are reduced as they are consumed by EVOH treated with it. Therefore, the used solution shall be discarded as waste, or may be recovered and recycled. For the latter, however, a suitable amount of fresh acidic substance and/or metal salt must be added to the used solution. Discarding the waste of the used solution as such is undesirable for environmental protection, and it requires some additional equipment for waste treatment. On the other hand, in case where the used solution is recovered and recycled, it also requires additional equipment for adding fresh acidic substance and/or metal salt to the used solution



and additional equipment for removing impurities such as typically oligomers from the used solution for obtaining products of stable quality. The conventional methods involve serious problems in that they require large-scale treating equipment and long treating time and therefore the production costs increase.

[0014]

For melt-extruding wet EVOH, proposed are a method of extruding it in melt at a specific level of energy (Japanese Patent Laid-Open No. 58500/1999); and a method of extruding it in melt under specific control of the cylinder temperature of the extruder used (Japanese Patent Laid-Open No. 58501/1999). However, these references are silent on the problem of how to control the water content of EVOH in melt extrusion.

[0015]

[Problems that the Invention is to Solve]

One object of the present invention is to provide a method for producing an EVOH resin that ensures efficient removal of alcohol not worsening the environment in and around working areas. Another object of the invention is to provide a method for producing pellets of the EVOH resin, of which the advantage is that it enables stable production and rapid washing of the pellets.

The EVOH resin pellets thus produced can be fed smoothly into extruders, enjoying stable extrusion and thermal stability

in long-run extrusion working lines.

[0016]

[Means for Solving the Problems]

We, the present inventors have assiduously studied, and have found that the problems noted above can be solved by providing a method for producing an EVOH resin that comprises a step of preparing an aqueous EVOH composition by contacting an alcohol-containing EVOH solution with water with letting the alcohol out of the system along with water, and a step of feeding the aqueous EVOH composition into an extruder and kneading it in melt therein.

[0017]

Specifically, one aspect of the invention is a method for producing an EVOH resin, which comprises

a step of introducing an EVOH solution that contains at least 50 parts by weight, relative to 100 parts by weight of EVOH therein, of an alcohol having a boiling point of not higher than 100°C, into an apparatus, and contacting it with water in the apparatus, thereby letting the alcohol out along with water and taking the resulting aqueous EVOH composition that contains from 0 to 10 parts by weight of the alcohol and from 10 to 1000 parts by weight of water, relative to 100 parts by weight of EVOH therein, out of the apparatus (step 1), and

a step of feeding the aqueous EVOH composition into an extruder, kneading it in melt therein, and then extruding the

copolymer out of the extruder (step 2).

[0018]

In the production method, the ethylene content of EVOH to be processed preferably falls between 3 and 70 mol% and the degree of saponification thereof is preferably at least 80 mol%. Also preferably, the alcohol to be used therein is methanol.

[0019]

Preferably in the step 1 in the production method, the EVOH solution is introduced into a vessel and contacted with water vapor in the vessel, thereby letting the alcohol out along with water vapor and taking the resulting aqueous EVOH composition out of the vessel. More preferably in this, the EVOH solution is continuously introduced into a column vessel and contacted with water vapor in the vessel. Even more preferably in this, the EVOH solution is introduced into the vessel through its upper part with water vapor through its lower part to thereby make the EVOH solution contacted with water vapor in countercurrent flow, and the resulting aqueous EVOH composition is taken out of the vessel through its lower part with the alcohol being let out through its upper part along with water vapor.

[0020]

Preferably in the step 2 in the production method, the temperature of the resin melt in the extruder falls between 70 and 170°C. Also preferably, the water content of the resin melt

just extruded out of the extruder falls between 5 and 40 % by weight. Also preferably, necessary water is fed into the extruder or excess water is removed from it to thereby control the water content of the resin in the extruder. Also preferably in the step 2, the aqueous EVOH composition is kneaded in melt in the extruder with at least one additive selected from carboxylic acids, boron compounds, phosphoric acid compounds, alkali metal salts and alkaline earth metal salts fed thereinto. More preferably, an aqueous solution of the additive is fed into the extruder. Also preferably, a wash is fed into the extruder and it is discharged from it through at least one site downstream the wash inlet site to thereby remove the saponification catalyst residue from the resin melt.

[0021]

Also preferably, the aqueous EVOH composition taken out of the apparatus in the step 1 in the production method is cut into pellets, and the resulting pellets are fed into the extruder in the step 2. More preferably, the pellets are dipped in a wash to remove the saponification catalyst residue from them, and then fed into the extruder in the step 2. Even more preferably, the pellets are continuously washed in a column vessel. Also preferably, the pellets are dipped in an aqueous solution containing at least one additive selected from carboxylic acids, boron compounds, phosphoric acid compounds, alkali metal salts and alkaline earth metal salts to thereby add the additive to

the pellets, and then they are fed into the extruder in the step 2.

[0022]

Also preferably, the aqueous EVOH composition taken out of the apparatus in melt in the step 1 in the production method is, not cut, fed into the extruder in the step 2. More preferably, the aqueous EVOH composition is, not cut, fed into the extruder in the step 2, and a wash is fed into the extruder and discharged from it through at least one site downstream the wash inlet site to thereby remove the saponification catalyst residue from the resin melt.

[0023]

The invention encompasses a method for producing EVOH resin pellets, which comprises cutting the EVOH resin that is extruded out of the extruder in the step 2 in the production method as above. Preferably, the pellets are, after cut, dried to have a water content of at most 1 % by weight.

[0024]

[Modes of Carrying out the Invention]

The method for producing an EVOH resin of the invention comprises a step of introducing an alcohol-containing EVOH solution into an apparatus, and contacting it with water in the apparatus thereby letting the alcohol out along with water and taking the resulting aqueous EVOH composition out of the apparatus (step 1), and a step of feeding the aqueous EVOH

composition into an extruder, kneading it in melt therein, and then extruding the copolymer out of the extruder (step 2). The EVOH resin is meant to indicate an EVOH resin composition finally obtained after various treatments of EVOH that is prepared through polymerization followed by saponification, for example, by washing EVOH, controlling the water content of EVOH and adding additives to EVOH. Naturally, it shall encompass the EVOH resin composition in the extruder and also the EVOH resin composition just after extruded out of the extruder in the step 2 of the method of the invention. Accordingly, the EVOH resin may contain water, various additives and impurities.

[0025]

In general, EVOH for use in the invention is obtained by saponifying an ethylene-vinyl ester copolymer. Its ethylene content generally falls between 3 and 70 mol%. For ensuring good melt moldability of the resin to give moldings with good gas barrier properties, the ethylene content of EVOH preferably falls between 10 and 60 mol%, more preferably between 20 and 55 mol%, most preferably between 25 and 55 mol%. The degree of saponification of the vinyl ester moiety in EVOH is generally at least 80 mol%, but preferably at least 95 mol%, more preferably at least 99 mol% to ensure moldings with good gas barrier properties.

[0026]

EVOH having an ethylene content of from 3 to 20 mol% is

preferred, as soluble in water, and an aqueous solution of EVOH of the type is an excellent coating material with good property capable of being formed into coating films with good barrier properties.

[0027]

EVOH having a degree of saponification of from 80 to 95 mol% may be used for improving the moldability and workability of the resin. Though it may be used alone, but is preferably blended with EVOH having a degree of saponification of higher than 99 mol%.

[0028]

In point of the production process, however, EVOH having an ethylene content of from 3 to 20 mol% and EVOH having a degree of saponification of from 80 to 95 mol% are both problematic in that the methanol solution of EVOH of either type is difficult to extrude and coagulate into strands in a coagulating bath. The invention has made it possible to readily coagulate EVOH of these types to stably produce their pellets. To that effect, the meaning of the invention is significant.

[0029]

In general, the melt moldability of EVOH having an ethylene content of smaller than 3 mol% is not good, and the waterproofness, the hot water resistance and the gas barrier properties at high humidity of EVOH of the type are often poor. On the other hand, the barrier properties and the printability of EVOH having an

ethylene content of larger than 70 mol% are often poor. The barrier properties, the yellowing resistance and the moisture resistance of EVOH having a degree of saponification of smaller than 80 mol% are often unsatisfactory.

[0030]

The method of producing EVOH for use in the invention is described concretely. To produce it, for example, ethylene is polymerized with a vinyl ester in any desired manner including solution polymerization, suspension polymerization, emulsion polymerization and bulk polymerization and in any desired mode of continuous or batchwise polymerization. One example of batchwise solution polymerization to produce the polymer is described, for which the polymerization condition is as follows.

[0031]

Solvent:

Alcohols having a boiling point of not higher than 100°C are used. In view of the solubility of ethylene-vinyl ester copolymers and EVOH therein and of the handlability thereof, such alcohols are used. The boiling point of the alcohols to be used must not be higher than 100°C, and the reason is because the alcohol of which the boiling point is lower than that of water is efficiently substituted with water in the process of substituting it with water. Preferably, the boiling point of the alcohols for use herein is not higher than 80°C, more preferably not higher than 70°C.



Alcohols having a boiling point of not higher than 100°C include, for example, methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol and t-butyl alcohol. Methyl alcohol is especially preferred for use herein.

[0032]

Catalyst:

Usable are azonitrile-type initiators such as 2,2-azobisisobutyronitrile, 2,2-azobis-(2,4-dimethylvaleronitrile), 2,2-azobis-(4-methoxy-2,4-dimethylvaleronitrile) and 2,2-azobis-(2-cyclopropylpropionitrile); and organic peroxide-type initiators such as isobutyryl peroxide, cumyl peroxyneodecanoate, diisopropyl peroxy carbonate, di-n-propyl peroxydicarbonate, t-butyl peroxyneodecanoate, lauroyl peroxide, benzoyl peroxide and t-butyl hydroperoxide.

[0033]

Vinyl ester:

Usable are vinyl esters of fatty acids (e.g., vinyl acetate, vinyl propionate, vinyl pivalate). Preferred is vinyl acetate. EVOH for use herein may contain a comonomer component of a vinylsilane compound in an amount of from 0.0002 to 0.2 mol%. The vinylsilane compound includes, for example, vinyltrimethoxysilane, vinyltriethoxysilane, vinyltri( $\beta$ -methoxyethoxy)silane and  $\gamma$ -methacryloxypropylmethoxysilane. Of those, preferred are

vinyltrimethoxysilane and vinyltriethoxysilane.

[0034]

The polymerization condition is as follows.

- (1) Temperature: 20°C to 90°C, preferably 40°C to 70°C.
- (2) Time: 2 to 15 hours, preferably 3 to 11 hours.
- (3) Degree of polymerization: 10 % to 90 %, preferably 30 % to 80 % relative to the vinyl ester used.
- (4) Polymerized resin content of the solution: 5 % to 85 %, preferably 20 % to 70 %.
- (5) Ethylene content of the copolymer: 3 to 70 mol%, preferably 10 to 60 mol%, more preferably 20 to 55 mol%, most preferably 25 to 55 mol%.

[0035]

Except for ethylene and vinyl esters, any other minor comonomers capable of copolymerizing with them may be present in the polymerization system. The comonomers include, for example,  $\alpha$ -olefins such as propylene, isobutylene,  $\alpha$ -octene and  $\alpha$ -dodecene; unsaturated acids such as acrylic acid, methacrylic acid, crotonic acid, maleic acid and itaconic acid, and their anhydrides, salts, or mono- or di-alkyl esters; nitriles such as acrylonitrile and methacrylonitrile; amides such as acrylamide and methacrylamide; olefin sulfonic acids such as ethylenesulfonic acid, allylsulfonic acid and methallylsulfonic acid, and their salts; alkyl vinyl ethers, vinyl ketones, N-vinylpyrrolidone, vinyl chloride and

vinylidene chloride.

[0036]

After the monomers have been polymerized for a predetermined period of time to give the intended copolymer having a predetermined degree of polymerization, a polymerization inhibitor may be added thereto, if desired. Then, the non-reacted ethylene gas is evaporated away, and the non-reacted vinyl ester is purged away. To purge the non-reacted vinyl ester, for example, the copolymer solution from which ethylene has been evaporated away is continuously run into a column filled with raschig rings, through the upper part of the column at a constant flow rate, while a vapor of an organic solvent, preferably an alcohol having a boiling point of not higher than 100°C, most preferably methanol is jetted into the column through its lower part, whereby a mixed vapor of the organic solvent and the non-reacted vinyl ester is run off from the column through its top, and the copolymer solution from which the non-reacted vinyl ester was removed is taken out of the column through its bottom.

[0037]

An alkali catalyst is added to the copolymer solution from which the non-reacted vinyl ester was removed, and the vinyl ester moiety of the copolymer is saponified. For this, employable is any of continuous or batchwise saponification. The alkali catalyst includes, for example, sodium hydroxide,

potassium hydroxide, and alkali metal alcoholates. One example of batchwise saponification is described, for which the condition is as follows.

- (1) Ethylene-vinyl ester copolymer content of the solution: 10 % to 50 %.
- (2) Reaction temperature: 30°C to 65°C.
- (3) Amount of catalyst: 0.02 to 1.0 equivalent (based on the vinyl ester moiety).
- (4) Time: 1 to 6 hours.

[0038]

The EVOH solution thus obtained generally contains at least 50 parts by weight, relative to 100 parts by weight of EVOH therein, of the alcohol having a boiling point of not higher than 100°C. The alcohol content of the solution is preferably at least 70 parts by weight, more preferably at least 80 parts by weight. Also preferably, the alcohol content is at most 1000 parts by weight, more preferably at most 500 parts by weight. Having the alcohol content falling within the range, the EVOH solution is well fluid and the EVOH resin is produced efficiently. The alcohol is preferably methanol.

The EVOH solution after saponification is not limited to the alcohol solution as above. If desired, it may contain any other solvent such as water, and may be in the form of a solution in such a mixed solvent. For adding water thereto, for example, referred to are the prior art methods mentioned above.

[0039]

In the step 1 of the invention, an EVOH solution containing at least 50 parts by weight, relative to 100 parts by weight of EVOH therein, of an alcohol having a boiling point of not higher than 100°C, such as that prepared in the manner as above, is introduced into an apparatus and contacted with water therein, thereby letting the alcohol out along with water and taking the resulting aqueous EVOH composition that contains from 0 to 10 parts by weight of the alcohol and from 10 to 1000 parts by weight of water, relative to 100 parts by weight of EVOH therein, out of the apparatus.

[0040]

The apparatus is not specifically defined. For example, the EVOH solution may be contacted with water in a vessel, or may be contacted with water in an apparatus for kneading such as extruder. Preferably, it is contacted with water in a vessel, more preferably with water vapor therein for mass-scale treatment.

[0041]

In one preferred embodiment of the step 1 of the invention, the EVOH solution containing at least 50 parts by weight, relative to 100 parts by weight of EVOH therein, of an alcohol having a boiling point of not higher than 100°C is introduced into a vessel and contacted with water vapor therein, thereby letting the alcohol out along with water vapor and taking the resulting

aqueous EVOH composition that contains from 0 to 10 parts by weight of the alcohol and from 10 to 500 parts by weight of water, relative to 100 parts by weight of EVOH therein, out of the vessel.

[0042]

The mode of contacting the EVOH solution with water vapor in a vessel is not specifically defined, and may be any of continuous or batchwise modes. The shape of the vessel to be employed for it is not also specifically defined. For continuous systems, however, preferred is a column vessel; and for batchwise systems, preferred is a tank vessel. From the viewpoint of production efficiency, preferred are continuous systems for industrial production. Examples of the column vessel are plate columns such as porous plate columns or bubble-cap towers, and packed columns such as those filled with a ring-type filler.

[0043]

The EVOH solution and water vapor introduced into a vessel are preferably contacted with each other in countercurrent flow therein, from the viewpoint of the efficiency of alcohol removal. For example, one preferred embodiment of the method comprises introducing an EVOH solution into a column vessel through its upper part and water vapor through its lower part so that the two are contacted with each other in countercurrent flow in the vessel, and taking the resulting aqueous EVOH composition out of the vessel through its lower part with the released alcohol being let out through the upper part of the vessel along with

water vapor. The alcohol vapor and water vapor having been thus let out through the upper part of the column vessel are condensed in a condenser and the resulting aqueous alcohol solution is taken out. If desired, it may be purified and recycled.

[0044]

Regarding the amount of water vapor to be introduced into the vessel, if it is too small, the alcohol removal efficiency will be low; but if too large, it will increase the production costs. Accordingly, the amount of water vapor to be introduced preferably falls between 0.3 and 30 times in terms of the ratio by weight to the amount of the EVOH solution introduced into the vessel, more preferably between 0.5 and 10 times, even more preferably between 0.7 and 5 times. The water vapor to be contacted with the EVOH solution may contain at most 10 parts by weight of an alcohol, relative to 100 parts by weight of the water vapor. However, for more efficient alcohol removal, it is desirable that the water vapor does not contain an alcohol.

[0045]

Preferably, the temperature in the vessel falls between 100 and 150°C. If the temperature in the vessel is lower than 100°C, the aqueous EVOH composition produced therein may not be well fluid, and will gel in the vessel or will clog the vessel. More preferably, the temperature is not lower than 110°C, even more preferably not lower than 120°C. On the other hand, if the temperature in the vessel is higher than 150°C, the EVOH

may deteriorate therein. More preferably, the temperature is not higher than 140°C.

[0046]

Regarding the pressure in the vessel, if it is too low, the alcohol removal efficiency will be low; but if too high, the temperature of the EVOH solution in the vessel will rise and EVOH will be thermally deteriorated. Accordingly, the pressure preferably falls between 1 and 6 kg/cm<sup>2</sup>, more preferably between 1.5 and 5 kg/cm<sup>2</sup>, even more preferably between 2 and 4 kg/cm<sup>2</sup>.

[0047]

In this method, the EVOH solution is kept in direct contact with water vapor in the vessel, and its alcohol content gradually decreases. In this stage, EVOH is in the form of a swollen paste, not gelled, and can be smoothly taken out of the vessel as it is still fluid.

[0048]

EVOH dissolves in a water/methanol mixed solvent under atmospheric pressure, for example, at 60°C to 70°C or so, but does not dissolve in a solvent of water alone under atmospheric pressure. However, we, the present inventors have found that, even when EVOH contains substantially water alone, it is still fluid in the presence of pressurized water vapor at a temperature not lower than 100°C. As a result, we have made it possible to continuously treat EVOH with ease, for example, in a column



vessel.

[0049]

The aqueous EVOH composition to be taken out of the vessel contains from 0 to 10 parts by weight of an alcohol and from 10 to 1000 parts by weight of water, relative to 100 parts by weight of EVOH therein, and it is still fluid. The alcohol content of the aqueous EVOH composition preferably falls between 0 and 5 parts by weight, more preferably between 0 and 1 part by weight, even more preferably 0 and 0.1 part by weight. As the alcohol content of the aqueous EVOH composition is lowered, alcohol vaporization is prevented in the post-treatment step of coagulating the composition, and the environment in and around the working areas can be kept good. In addition, even when the pellets of the EVOH composition are washed at an elevated temperature for removing the saponification catalyst residue, they do not stick together. Therefore, the temperature of the wash can be elevated, and, as a result, the washing speed can be increased.

[0050]

The water content of the aqueous EVOH composition falls between 10 and 1000 parts by weight. If the water content is smaller than 10 parts by weight, the fluidity of the composition in the vessel will be poor. Preferably, the water content is at least 30 parts by weight, more preferably at least 50 parts by weight. However, if the water content is larger than 1000

parts by weight, it is problematic in that the EVOH composition could not be stably coagulated into strands. If so, in addition, the pellets produced by cutting the composition in melt often fuse together and their shape is not homogeneous. Preferably, the water content is at most 500 parts by weight, more preferably at most 200 parts by weight.

[0051]

The aqueous EVOH composition obtained in the manner as herein generally contains from 0.1 to 5 % by weight of an alkali metal salt in terms of the metal, and also salts as by-products and other impurities.

[0052]

The method for producing an EVOH resin of the invention comprises another step of feeding the aqueous EVOH composition prepared in the previous step 1, into an extruder, kneading it in melt therein, and then extruding the resin melt out of the extruder (step 2). In the method, the means of feeding the aqueous EVOH composition having been led out of the apparatus in the step 1, into the extruder in the step 2 is not specifically defined. For example, the aqueous EVOH composition led out of the apparatus in the step 1 may be, after cut into pellets, fed into the extruder in the step 2; or not cut, it may be directly fed thereinto while still in melt.

[0053]

The embodiment of feeding the aqueous EVOH composition

having been led out of the apparatus in the step 1, into the extruder in the step 2, after cut into pellets, is described. In this embodiment, the aqueous EVOH composition led out of the apparatus in the step 1 is cut into pellets. The method of cutting it into pellets is not specifically defined. For example, the aqueous EVOH composition in melt may be extruded into strands in a coagulating bath, and the thus-coagulated strands are cut; or the aqueous EVOH composition may be directly cut in melt.

[0054]

In the method of extruding it into strands in a coagulating bath followed by cutting them, the aqueous EVOH composition taken out of the vessel is first extruded in a coagulating bath through nozzles to be strands having a desired diameter. In this step, if the water content of the aqueous EVOH composition is too high, water will separate from the composition and the thus-separated water will be jetted out of nozzles to interfere with continuous formation of EVOH strands. Therefore, it is desirable to previously remove water from the aqueous EVOH composition by treating it in a kneader or the like, and thereafter the composition is extruded out through nozzles into strands in a coagulating bath to coagulate them. The kneader may be composed of a cylinder equipped with a liquid-discharging port, and a screw fitted therein.

[0055]

The coagulating bath is water, but may contain a small

amount of an alcohol. In the conventional method in which a methanol solution or water/methanol mixed solution of EVOH is extruded in a coagulating bath, methanol must be added to the coagulating bath so as to lower the specific gravity of the bath for preventing the extruded strands from floating in the bath before they are coagulated therein. In the present invention, however, the coagulating bath to be used may be water alone not containing an alcohol, since the coagulation rate of the strands extruded therein is high. The method of the invention is therefore superior to the conventional method, not worsening the environment in and around the working areas.

[0056]

Preferably, the temperature of the coagulating bath falls between 0°C and 50°C, and that of the molten aqueous EVOH composition to be extruded in the bath falls between 100°C and 150°C. The temperature difference enables the coagulation of the aqueous EVOH composition extruded in the bath in a short time. More preferably, the temperature of the coagulating bath falls between 0°C and 30°C, and that of the molten aqueous EVOH composition to be extruded in the bath falls between 110°C and 140°C. The coagulated strands are cut with a cutter into pellets. The cutter is preferably a strand cutter.

[0057]

In case where the aqueous EVOH composition taken out of the vessel is directly out in melt, a hot cutting system or an

under-water cutting system is preferred for the method. The nozzles through which the composition is extruded preferably have an orifice diameter of from 2 to 5 mm $\phi$  ( $\phi$  indicates a diameter, and the same shall apply hereinunder), as the pellets thus formed are easy to handle. Fig. 1 shows one example of a hot cutter usable in a hot cutting system. In this, 1 indicates an aqueous EVOH composition inlet port; 2 indicates a die; 3 indicates a rotary blade; 4 indicates a rotation axis; 5 indicates a cutter box; 6 indicates a cooling water inlet port; 7 indicates cooling water; 8 indicates a water membrane; 9 indicates a pellets take-out port; and 10 indicates cooling water and pellets.

[0058]

If the water content of the aqueous EVOH composition is too high, water will separate from the aqueous EVOH composition and the thus-separated water will be jetted out of nozzles to interfere with stable cutting of the composition. Therefore, like in the case of cutting strands as above, it is also desirable to previously remove water from the EVOH by treating it in a kneader or the like, and thereafter the composition is jetted out through nozzles and out into pellets.

[0059]

The EVOH pellets thus obtained generally contain the residue of the saponification catalyst, alkali metal salts. If the catalyst residue content of the pellets is too high, it causes a quality problem of yellowing. Therefore, it is desirable to

remove the catalyst residue by washing the pellets. The washing method is not specifically defined. For example, the pellets are washed by dipping them in water or an aqueous acid solution of acetic acid or the like.

[0060]

The washing temperature may fall between 0 and 95°C. From the viewpoint of higher washing efficiency, the washing temperature is preferably higher. However, if too high, it is unfavorable as causing fusion of pellets. The lowermost limit of the washing temperature is preferably at least 20°C, more preferably at least 30°C, most preferably at least 40°C. In the conventional method, the washing temperature falls between about 25°C and 30°C or so. Compared with this, the washing temperature in the method of the invention may be high, which is another characteristic feature of the invention. The uppermost limit of the washing temperature is preferably at most 80°C, more preferably at most 70°C. After thus washed, the alkali metal salt content of the EVOH pellets is preferably at most 0.05 % by weight in terms of the metal, more preferably at most 0.03 % by weight.

[0061]

Without being washed in that manner, the pellets may be washed in the extruder in the next step 2. Needless-to-say, the pellets thus washed in the manner as above may be further washed in the extruder in the next step 2. The method of washing

them in the step 2 will be described hereinunder.

[0062]

Preferably, at least one additive selected from the group consisting of carboxylic acids, boron compounds, phosphoric acid compounds, alkali metal salts and alkaline earth metal salts is added to the EVOH pellets for improving the quality such as the thermal stability of the pellets. The method of adding it to the pellets is not specifically defined, and any known method is employable. For example, the pellets are dipped in an aqueous solution containing the additives so that they adsorb it.

[0063]

Examples of carboxylic acids usable herein are oxalic acid, succinic acid, benzoic acid, citric acid, acetic acid and lactic acid. Preferably used is acetic acid, as inexpensive and easily available. Regarding the carboxylic acid content of the dry EVOH pellets of the invention, if it is too small, the pellets will be yellowed while molded in melt; but if too large, interlayer adhesion of the EVOH moldings will be poor. Therefore, the carboxylic acid content of the dry EVOH pellets of the invention preferably falls between 10 and 5000 ppm. The lowermost limit of the carboxylic acid content is preferably at least 30 ppm, more preferably at least 50 ppm. The uppermost limit of the carboxylic acid content is preferably at most 1000 ppm, more preferably at most 500 ppm.

[0064]

Examples of boron compounds usable herein are boric acids, borates, salts of boric acids, and boron hydrides, which, however, are not limitative. Concretely, boric acids include orthoboric acid, metaboric acid and tetraboric acid; borates include triethyl borate and trimethyl borate; and salts of boric acids include alkali metal salts and alkaline earth metal salts of various boric acids mentioned above, and borax. Of those compounds, preferred is orthoboric acid (this is simply referred to as boric acid). Regarding the boron compound content of the dry EVOH resin pellets of the invention, if it is too small, the thermal stability of the pellets is not so good; but if too large, the pellets will often gel and their moldability is often poor. Therefore, the boron compound content preferably falls between 10 and 2000 ppm in terms of boron, more preferably between 50 and 1000 ppm.

[0065]

Examples of phosphoric acid compounds usable herein are various acids such as phosphoric acid and phosphorous acid and their salts. Any phosphoric acid of any type of primary phosphates, secondary phosphates and tertiary phosphates may be added to the EVOH pellets, and its cation is not specifically defined. Preferred are alkali metal salts and alkaline earth metal salts. Above all, sodium dihydrogenphosphate, potassium dihydrogenphosphate, disodium hydrogenphosphate and dipotassium hydrogenphosphate are preferred for the phosphoric



anion of the alkaline earth metal salts is not specifically defined, for which, however, preferred are acetates and phosphates. The alkaline earth metal salt content of the dry EVOH resin pellets of the invention preferably falls between 10 and 1000 ppm, more preferably between 20 and 500 ppm in terms of the metal. If the alkaline earth metal salt content thereof is smaller than 10 ppm, the long-run workability of the EVOH resin may be poor; but if larger than 1000 ppm, the EVOH resin may be much yellowed when molded in melt.

[0068]

If desired, the additive may be added to the EVOH resin in the extruder in the next step 2, not added thereto in the step 1. Also if desired, some specific component is added to the EVOH resin in the step 1, and some others may be added thereto in the extruder in the step 2. The method of adding the additive to the EVOH resin in the step 2 will be described hereinunder.

[0069]

The method of washing the aqueous EVOH composition pellets, and the method of adding the additive to the aqueous EVOH composition pellets are not specifically defined, for which, for example, employable are any of batch-process units or continuous-process units. Especially preferred is a method of continuously feeding and processing the pellets in a column vessel in view of the productivity. The washing operation and the additive-adding operation may be effected at the same time

in one and the same processing column, or may be effected separately in different processing columns.

[0070]

After optionally washed and/or mixed with an additive in the manner as above, the resulting, aqueous EVOH composition pellets are fed into an extruder for the next step 2.

[0071]

Not cut in the manner as above, the aqueous EVOH composition having been led out of the apparatus in the step 1 may be directly, while still in melt, fed into an extruder for the next step 2. In this case, the operation of washing the composition and the operation of adding the additive to the composition are preferably effected in the step 2. Amorphous crumbs of solidified EVOH paste may also be fed into an extruder for the step 2.

[0072]

In the step 2 of the invention, the aqueous EVOH composition prepared in the previous step 1 is fed into an extruder, kneaded in melt therein, and then extruded out of the extruder. The step 2 is described below.

[0073]

Before fed into the extruder in the step 2, the water content of the aqueous EVOH composition is preferably at least 10 % by weight, more preferably at least 30 % by weight, even more preferably at least 50 % by weight. Also preferably, the water

content of EVOH before fed into the extruder in the step 2 is at most 1000 % by weight, more preferably at most 500 % by weight, even more preferably at most 200 % by weight. Having the water content falling within the preferred range before fed into the extruder, the aqueous EVOH composition may be kneaded in melt in the extruder at a temperature lower than the melting point of the dry EVOH, and can be stably extruded out of the extruder not thermally degraded therein.

[0074]

If the water content of the aqueous EVOH composition is lower than 10 % by weight before fed into the extruder, preventing the thermal degradation of EVOH in the extruder will be unsatisfactory. If, on the other hand, the water content of the aqueous EVOH composition is higher than 1000 % by weight, water will separate from EVOH and the amount of the EVOH composition fed into the extruder will thereby fluctuate, and, as a result, will have some negative influence on the extrusion stability of the resin melt in the step 2.

[0075]

Preferably, the resin temperature in the extruder in the step 2 falls between 70 and 170°C. If the resin temperature is lower than 70°C, the aqueous EVOH composition may not completely melt. In addition, when at least one additive selected from carboxylic acids, boron compounds, phosphoric acid compounds, alkali metal salts and alkaline earth metal salts

is added to the resin composition, its effect for improving the dispersibility may likely become insufficient if the resin temperature is too low. More preferably, the resin temperature in the extruder is not lower than 80°C, even more preferably not lower than 90°C. If, however, the resin temperature is higher than 170°C, EVOH may be thermally degraded. In addition, when the additive is added to the resin composition as its aqueous solution, much water will evaporate if the resin temperature is higher than 170°C. If so, the aqueous solution of the additive could not have the desired water content and may not well mix with the aqueous EVOH composition. Preferably, the resin temperature is not higher than 150°C, more preferably not higher than 130°C. The method of controlling the resin temperature is not specifically defined. For example, one preferred method for it is to suitably control the cylinder temperature in the extruder. In the present invention, the resin temperature denotes a temperature detected by the temperature sensor provided at the cylinder of the extruder, and detected around the discharge portion at the tip of the extruder.

[0076]

In the step 2, the saponification catalyst residue still remaining in EVOH can be washed away in the extruder. Concretely, after the aqueous EVOH composition to be processed is fed into the extruder, a wash is fed thereinto through at least one site of the extruder for washing the resin therein, and it is discharged

from the extruder through at least one site downstream the wash inlet site. This method is favorable as it enables efficient and space-saving washing of the resin. In this case, the saponification catalyst residue remaining in EVOH to be fed into the extruder is preferably an alkali metal salt.

[0077]

Preferably, the alkali metal salt content of the aqueous EVOH composition to be fed into the extruder in the step 2 falls between 0.1 and 5 % by weight in terms of the metal, more preferably at least 0.2 % by weight, even more preferably at least 0.5 % by weight. Also more preferably, it is at most 4 % by weight, even more preferably at most 3 % by weight. If the content is smaller than 0.1 % by weight, any other conventional washing method may realize good space-saving for the case, and the specific washing method of the invention will be meaningless for it. On the other hand, if the content is larger than 5 % by weight, it is also undesirable as requiring an extruder having a large aspect ratio L/D and increasing the washing cost.

[0078]

Also preferably, the alkali metal salt content of the EVOH resin washed in the manner as above is at most 0.05 % by weight in terms of the metal, more preferably at most 0.04 % by weight, even more preferably at most 0.03 % by weight. If the content is larger than 0.05 % by weight, it is undesirable as the thermal stability of EVOH is low.

[0079]

The wash to be used herein is not specifically defined so far as it can remove the saponification catalyst residue from EVOH. For example, preferred for it is an aqueous solution of an acid having a pKa at 25°C of at least 3.5. An aqueous solution of an acid having a pKa at 25°C of smaller than 3.5 is undesirable, as the EVOH resin washed with it may lose good yellowing resistance and good delamination resistance. For the acid of the type having a pKa of at least 3.5, preferred are carboxylic acids, and more preferred is acetic acid as inexpensive. The acetic acid concentration of the aqueous acetic acid solution for the wash preferably falls between 0.01 and 10 g/liter, more preferably between 0.1 and 2 g/liter. Also preferably, the amount of the wash to be introduced into the extruder falls between 0.1 and 100 liters/kg of resin.

[0080]

The method of introducing the wash into the extruder is not specifically defined, and may be any and every conventional one. For example, the wash may be introduced thereinto under pressure with a plunger pump. The method of discharging the wash from the extruder is not also specifically defined, so far as a discharge unit disposed downstream the wash inlet site of the extruder discharges the wash out of the extruder. For the discharge unit, for example, preferred is a water-discharging slit or hole. If desired, plural wash inlets or plural wash

discharge sites may be disposed in the extruder.

[0081]

Preferably in the invention, the aqueous EVOH composition is, after washed in the extruder in the step 2 in the manner as above, or not washed so, dewatered or degassed therein. Concretely for it, water and/or water vapor is discharged through at least one site of the extruder. The method of discharging it is not specifically defined. For example, water and/or water vapor may be discharged through a dewatering slit or hole or a vent disposed through the cylinder in the extruder. The dewatering slit is preferably a wedge wire slit or screen mesh slit for dewatering. The vent may be a vacuum vent for removing water vapor under reduced pressure, or an open vent for removing water vapor under atmospheric pressure.

[0082]

Of those, preferred is a dewatering slit or hole. These may discharge any of water and water vapor, and therefore enable efficient water removal from resin of high water content. In this point, they are more effective than a vent that may generally discharge water vapor only. In case where water vapor is discharged through a vent, resin will often deposit around its mouth and the resin deposit around it is aged and contaminates the resin in the extruder. In view of this, a dewatering slit or hole is preferred to a vent. On the other hand, when a dewatering hole is used for water or water vapor removal, a resin

melt may be forced out through it. In this point, a dewatering slit is preferred to such a dewatering hole.

[0083]

For dewatering the aqueous EVOH resin, one dewatering unit may be used alone, or plural dewatering units of the same type may be used, or plural dewatering units of different types may be combined. For example, water is first removed from resin of high water content in some degree through a dewatering slit, and thereafter the thus-dewatered resin may be further dewatered through a vent disposed downstream the dewatering slit.

[0084]

The dewatering operation mentioned above is for controlling the water content of the EVOH resin being processed in the extruder and after extruded out of it. In order to prevent the water content of the EVOH resin from being too much lowered, it is desirable to supply water into the extruder in addition to the dewatering operation or without effecting the dewatering operation. The method of supplying water to the extruder is not specifically defined. For it, for example, used is a plunger pump under pressure.

[0085]

Preferably, the water content of the EVOH resin just extruded out of the extruder in the step 2 falls between 5 and 40 % by weight, more preferably between 5 and 35 % by weight. If the water content of the EVOH resin just extruded out of the



extruder is larger than 40 % by weight, water may separate from EVOH and may foam the EVOH strands extruded out of the extruder. On the other hand, if the water content of the EVOH resin just extruded out of the extruder is smaller than 5 % by weight, EVOH may be thermally degraded in the extruder and may be often yellowed.

[0086]

After the EVOH resin is optionally washed and its water content is optionally controlled in the extruder, at least one additive selected from carboxylic acids, boron compounds, phosphoric acid compounds, alkali metal salts and alkaline earth metal salts may be added thereto for improving the properties of the EVOH resin. The preferred range of the amount of the additive is mentioned below. One selected from the additive compounds as above may be added alone to the EVOH resin, but two or more of them may be added thereto all at a time depending on their use. For the effect and the preferred amount of the additives, referred to are those mentioned hereinabove in the section relating to the treatment of the aqueous EVOH composition pellets prepared in the step 1.

[0087]

Adding the additive to the EVOH resin in the extruder is advantageous as producing an extremely uniform resin melt. This embodiment ensures good EVOH resin. Concretely, the advantages of the good EVOH resin produced in the embodiment are that the

resin does not require a large motor torque and does not increase the torque change in the extruder used in extrusion; its extrusion stability is good, its yellowing resistance is good, it is well processed even in long-run molding lines, its moldings have few gels and hard spots, and it deposits little on the die in the extruder used. When the additive is added to the EVOH resin in the extruder in the invention, it is desirable that the additive is supplied into the extruder in the site in which the EVOH resin is in melt. Adding the additive to the EVOH resin in that condition in the extruder enhances the effect of the invention. In particular, it is more desirable that the additive is added to the EVOH resin melt that contains water. Preferably, the extruder is equipped with a kneading portion. More preferably, the additive is added to the EVOH resin in the kneading portion of the extruder, as it can be uniformly mixed with the EVOH resin.

[0088]

Except the above-mentioned alkali metal salts and alkaline earth metal salts serving as the additive, also usable herein are other metal salts of Group 4 of the Periodic Table.

[0089]

The mode of adding the additive to the EVOH resin is not specifically defined. For example, the additive may be fed into the extruder in any form of dry powder of itself, paste in solvent, suspension in liquid, or solution in solvent. Of those, especially preferred is the additive solution in solvent as

ensuring uniform dispersion of the additive in the EVOH resin. The solvent for the solution is not specifically defined, for which, however, preferred is water. The advantages of water for the solvent are that it well dissolves the additive, and it is inexpensive, easy to handle and safe in working operations. Preferably, the additive is fed into the extruder through one or more sites.

[0090]

In case where a solution of the additive is added to the EVOH resin, its amount is preferably at least 1 part by weight, more preferably at least 3 parts by weight, even more preferably at least 5 parts by weight relative to 100 parts by weight of the EVOH resin in dry. Also preferably, its amount is at most 50 parts by weight, more preferably at most 30 parts by weight, even more preferably at most 20 parts by weight relative to 100 parts by weight of the EVOH resin in dry. If the amount of the solution added is smaller than 1 part by weight, the concentration of the solution must be high. However, it is unfavorable since the additive of such a thick solution may not well disperse in the EVOH resin. On the other hand, if the amount of the solution added is larger than 50 parts by weight, it is also unfavorable since the water content of EVOH may be difficult to control and water may separate from EVOH in the extruder.

[0091]

In the conventional method of dipping EVOH resin pellets

in a solution of the additive as above, products of good quality are difficult to obtain from the crumbed deposit of EVOH resin. Overcoming the problem, the present invention has made it possible to uniformly add the additive even to the EVOH resin of the type, thereby realizing the production of EVOH resin products of good and stabile quality.

[0092]

The method of pelletizing the EVOH resin extruded out of the extruder in the step 2 is not specifically defined. For example, the resin composition is extruded into strands in a coagulating bath through the die of the extruder, and the strands may be cut into pellets having a predetermined length. For easy handlability of the pellets, the aperture of the die preferably falls between 2 and 5 mm $\phi$  ( $\phi$  indicates "diameter", and the same shall apply hereinafter); and the strands are cut into pellets preferably having a length of from 1 to 5 mm or so. A hot cut system and an under-water cut system are also preferred examples of the pelletization.

[0093]

The pellets are generally dried. After dried, the water content of the EVOH resin pellets is preferably at most 1.0 % by weight, more preferably at most 0.5 % by weight. The drying method is not also specifically defined, for which, however, preferred is ventilation drying or fluidized drying. As the case may be, multi-stage drying of a combination of some different

drying modes may also be employed herein. Especially preferred is a method of first drying the pellets in a mode of fluidized drying and further drying them in a mode of ventilation drying.

[0094]

In the conventional processing method of dipping EVOH resin pellets in a treating solution that contains the additive as above, the water content of the processed EVOH resin pellets generally falls between 40 and 70 % by weight or so. In the processing method of the invention, however, the water content of the EVOH resin just extruded out of the extruder may be controlled in any desired manner. Preferably, the water content of the EVOH resin just extruded out of the extruder falls between 5 and 40 % by weight. Accordingly, in the invention, EVOH resin pellets having a smaller water content than those in the conventional method can be obtained. The pellets are favorable as reducing the energy consumption in the process of drying them.

[0095]

In particular, EVOH pellets having a water content of larger than 40 % by weight will often fuse together when dried at a temperature of 100°C or higher. From this viewpoint, the processing method of the invention in which EVOH is melted in an extruder and the additive as above is added thereto in the extruder is favorable.

[0096]

If desired, the EVOH resin pellets obtained in the method

of the invention may be blended with any other EVOH that differs from them in the degree of polymerization, the ethylene content and the degree of saponification, and the resulting resin blend may be molded in melt. Also if desired, any other additives may be suitably added to the pellets. The additives include, for example, plasticizer, stabilizer, surfactant, colorant, UV absorbent, antistatic agent, drying agent, crosslinking agent, metal salt, filler, and reinforcing agent such as fibers. The EVOH resin pellets of the invention do not require a large motor torque and do not increase the torque change in the extruder used in extrusion, and their extrusion stability is good. Therefore, they are especially favorable for extrusion molding as the amount of the lubricant to be used in molding them may be greatly reduced or may be completely omitted, depending on their applications. However, this does not restrict the use of lubricant in molding the EVOH resin pellets of the invention.

[0097]

The EVOH resin pellets thus obtained in the invention can be molded in melt, for example, into various moldings such as films, sheets, containers, pipes and fibers. The moldings of the invention are especially favorable for wrapping and packaging various objects.

[0098]

[Example]

The invention is described in more detail with reference

to the following Examples, which, however, are not intended to restrict the scope of the invention. Unless otherwise specifically indicated, "%" and "part" are all by weight.

[0099]

(1) Measurement of Water Content:

20 g of a sample, EVOH is taken in a well-dried weighing bottle, and dried in a hot air drier at 120°C for 24 hours. From the weight change of EVOH before and after dried, the water content of EVOH is obtained according to the following formula (1):

$$\text{Water Content (\% by weight)} = (\text{weight before dried} - \text{weight after dried}) / (\text{weight before dried}) \times 100 \quad (1)$$

[0100]

(2) Quantitative Determination of Minor Components added:

The minor components added to EVOH are quantitatively determined according to the following methods.

(2-a) Quantitative Determination of Carboxylic Acid:

20 g of a sample, dry pellets is put into 100 ml of ion-exchanged water, and extracted under heat at 95°C for 6 hours. The resulting extract is titered for neutralization with aqueous 1/50 N NaOH solution, using phenolphthalein as an indicator, to determine the carboxylic acid content of the sample.

(2-b) Quantitative Determination of Alkali Metal Salt and Alkaline Earth Metal Salt:

10 g of a sample, dry pellets is put into 50 ml of aqueous 0.01 N HCl solution, and stirred at 95°C for 6 hours. After

thus stirred, the aqueous solution is analyzed through ion chromatography, in which the column used is Yokogawa Electric's ICS-C25, and the eluent used is an aqueous solution containing 5.0 mM tartaric acid and 1.0 mM 2,6-pyridinedicarboxylic acid. The quantitative determination is based on the calibration curves of the respective, aqueous metal chloride solutions. The thus-obtained data of the alkali metal salt and the alkaline earth metal salt in the dry pellets are represented in terms of the metal.

(2-c) Quantitative Determination of Boron Compound:

An aqueous  $\text{Na}_2\text{CO}_3$  solution is added to a sample, dry pellets, and ashed in a platinum crucible at  $600^\circ\text{C}$ . The ashed sample is dissolved in hydrochloric acid, and analyzed through ICP emission spectrometry. The thus-obtained boron compound content of the sample is represented in terms of the boron.

(2-d) Quantitative Determination of Phosphoric Acid Compound:

10 g of a sample, dry pellets is put into 50 ml of aqueous 0.01 N HCl solution, and stirred at  $95^\circ\text{C}$  for 6 hours. After thus stirred, the aqueous solution is analyzed through ion chromatography, in which the column used is Yokogawa Electric's ICS-A23, and the eluent used is an aqueous solution containing 2.5 mM sodium carbonate and 1.0 mM sodium hydrogencarbonate. The quantitative determination is based on the calibration curve of an aqueous phosphoric acid solution. From the thus-obtained data of the phosphate ions, the phosphoric acid compound content



of the sample is obtained in terms of the phosphate radical.

[0101]

(3) Melt Index (MI):

Measured according to ASTM-D1238 using a melt indexer, at a temperature of 190°C under a load of 2160 g.

[0102]

(4) Test for single-layer Film Formation (motor torque and torque change in extruder):

Using an extruder mentioned below, a single layer of a sample, EVOH resin is formed. While the sample, EVOH resin pellets is in the extruder, the motor torque and the torque change are measured.

The details of the extruder are as follows:

Extruder: GT-40-A (by Research Laboratory Of Plastic Technology Co., Ltd.),

Type: single-screw extruder (with no vent),

L/D: 26,

CR: 3.5,

Diameter: 40 mmφ,

Screw: single-thread full-flight screw made of surface-nitrided steel,

Screw revolution: 40 rpm,

Motor: by Sumitomo Heavy Industry Ltd.; DC motor, SCR-DC218B, motor capacity DC 7.5 KW (rated current 45 A),

Heater: quartered type,

Die width: 300 mm,

Resin temperature in die: 240°C

Take-up speed: 10 m/min.

[0103]

Example 1:

An outline of the process of Example 1 is shown in Fig. 2. An EVOH solution containing 100 parts by weight of EVOH having an ethylene content of 32 mol% and a degree of saponification of 99.5 mol%, 100 parts by weight of methanol, 50 parts by weight of water and 2 parts by weight, in terms of sodium, of sodium acetate was continuously introduced into the 10-tier plate column 11 having a column diameter of 0.3 m, at its uppermost tier through the EVOH solution supply duct 21 at a feed rate of 52 kg/hr, while water vapor was jetted thereinto at the lowermost tier of the column through the water vapor supply duct 20 at a flow rate of 86 kg/hr, so that the EVOH solution was contacted with water vapor in countercurrent flow in the column. The temperature in the column was 130°C, and the pressure therein was 3 kg/cm<sup>2</sup>. The methanol vapor and water vapor led out of the column through its top via the vapor discharge duct 22 was condensed in the condenser 12, and the resulting aqueous methanol solution was recovered. The aqueous EVOH composition thus produced was continuously taken out of the column through its bottom via the aqueous composition take-out duct 23. This contained 0.05 parts by weight of methanol, 105 parts by weight

of water and 2 parts by weight, in terms of sodium, of sodium acetate, relative to 100 parts by weight of EVOH therein.

[0104]

Next, the aqueous EVOH composition was led into the kneader 13 equipped with a discharge port 28 and having a diameter of 50 mm and a length of 660 mm ( $L/D = 13.2$ ), at a feed rate of 41 kg/hr. The screw revolution in the kneader was 100 rpm. The aqueous EVOH composition thus led out through the discharge port contained 0.03 parts by weight of methanol, 63 parts by weight of water (water content, 39 %) and 1.2 parts by weight, in terms of sodium, of sodium acetate relative to 100 parts by weight of EVOH therein, and its temperature was 118°C. Next, this was extruded out through a die with six 3-mm $\phi$  holes, and cut with the hot cutter 14 into pellets (A). The hot cutter has four blades, and it was spaced from the die by 0.05 mm. The cutter blade revolution was 1200 rpm.

[0105]

The resulting pellets (A) were fed into the column vessel 15 having a diameter of 0.8 m and a height of 4 m, through its top via the pellet supply duct 24 at a feed rate of 33 kg/hr. On the other hand, an aqueous acetic acid solution (0.5 g/liter, 50°C) was fed into the vessel through its lower part via the solution supply duct 26 at a feed rate of 500 liters/hr. With that, the pellets were contacted with the aqueous acetic acid solution in countercurrent flow in the vessel. The aqueous

acetic acid solution was discharged out of the vessel through the solution discharge duct 25, while the washed pellets (B) were continuously taken out through the bottom of the vessel via the pellet take-out duct 27. The pellets (B) had a water content of 39 %, and still contained 0.002 % by weight, in terms of sodium, of sodium acetate. While washed, the pellets did not fuse together.

[0106]

Next, the pellets (B) were put into the twin-screw extruder 16. The resin temperature around the take-out port was 100°C. At the take-out side of the extruder, disposed was a minor component supply unit 31 as in Fig. 3. Through the supply unit 31, an aqueous treating solution comprising aqueous acetic acid/boric acid/sodium acetate/magnesium acetate/potassium dihydrogenphosphate was fed into the extruder. The feed rate of EVOH is 10.7 kg/hr (containing water), and the feed rate of the treating solution was 0.65 liters/hr. Precisely, the aqueous treating solution contained 4.3 g/liter of acetic acid, 15 g/liter of boric acid, 4.6 g/liter of sodium acetate, 3.0 g/liter of magnesium acetate tetrahydrate, and 1.4 g/liter of potassium dihydrogenphosphate. The details of the twin-screw extruder are mentioned below.

Type: twin-screw extruder,

L/D: 45.5,

Diameter: 30 mmφ,

Screw: uniaxial full engaging type,

Screw revolution: 300 rpm,

Cylinder temperature: 100°C,

Die temperature: 105°C,

Number of die holes: 5 (3 mmφ).

[0107]

The constitution of the twin-screw extruder is shown in detail in Fig. 3. The extruder comprises a raw material supply unit 29, a dewatering unit 30, and a minor component supply unit 31, and the dewatering unit is equipped with a wedge wire-type dewatering slit 33. For the screws, a full-flight screw 34 is combined with a reverse-flight screw 35, as illustrated. At the tip of the cylinder, disposed is a temperature sensor 32.

[0108]

The EVOH resin melt thus processed in the extruder was cut with the hot cutter 17 into pellets (C). The water content of the pellets (C) was 20 % by weight. The thus-obtained pellets (C) were dried in the fluidized drier 18 at 90°C for 15 hours, and then in the ventilation drier 19 at 105°C for 15 hours. Their water content reduced to 0.2 % by weight. After thus dried, the acetic acid content of the EVOH resin pellets (D) was 300 ppm, the boron compound content thereof was 270 ppm in terms of boron, and the phosphoric acid compound content thereof was 98 ppm in terms of phosphate radical. Regarding the alkali metal salt content of the pellets, the potassium salt content thereof

was 40 ppm in terms of metal, and the sodium salt content thereof was 130 ppm in terms of metal. Regarding the alkaline earth metal content of the pellets, the magnesium salt content thereof was 35 ppm in terms of metal. MI of the pellets was 1.5 g/10 min.

[0109]

The dry pellets (D) were formed into a single-layer film. While they were in the extruder for single-layer film formation, the motor torque and the torque change were measured. The motor torque for film extrusion was 210 kg·cm; and the torque change was 45 kg·cm.

[0110]

Example 2:

The pellets (A) of Example 1 were fed into the column vessel having a diameter of 0.8 m and a height of 4 m through its top at a feed rate of 33 kg/hr. On the other hand, an aqueous treating solution comprising acetic acid/sodium acetate/magnesium acetate/potassium dihydrogenphosphate (50°C) was fed into the vessel through its lower part at a feed rate of 500 liters/hr. For its details, the treating solution contained 1.7 g/liter of acetic acid, 0.67 g/liter of sodium acetate, 1.84 g/liter of magnesium acetate tetrahydrate and 0.77 g/liter of potassium dihydrogenphosphate. The treated pellets were continuously taken out through the bottom of the vessel. The pellets had a water content of 39 %.

[0111]

Next, the pellets were put into a twin-screw extruder, of which the constitution is the same as in Fig. 3 except that the screw at the site for minor component supply was changed to a full-flight screw. The resin temperature around the take-out port was 100°C; and the feed rate of EVOH was 10.7 kg/hr (containing water). No minor component was fed into the extruder. After extruded out, the EVOH resin pellets had a water content of 18 % by weight. The thus-obtained pellets were dried in the fluidized drier at 90°C for 15 hours, and then in the ventilation drier at 105°C for 15 hours. Their water content reduced to 0.2 % by weight. After thus dried, the acetic acid content of the EVOH resin pellets was 200 ppm, and the phosphoric acid compound content thereof was 90 ppm in terms of phosphate radical. Regarding the alkali metal salt content of the pellets, the potassium salt content thereof was 35 ppm in terms of metal, and the sodium salt content thereof was 120 ppm in terms of metal. Regarding the alkaline earth metal content of the pellets, the magnesium salt content thereof was 60 ppm in terms of metal. MI of the pellets was 12 g/10 min.

[0112]

The dry pellets were formed into a single-layer film. While they were in the extruder for single-layer film formation, the motor torque and the torque change were measured. The motor torque for film extrusion was 185 kg·cm; and the torque change

was 30 kg/cm.

[0113]

Example 3:

An EVOH solution containing 100 parts by weight of EVOH having an ethylene content of 35 mol% and a degree of saponification of 99.5 mol%, 100 parts by weight of methanol, 50 parts by weight of water and 1.5 parts by weight, in terms of sodium, of sodium acetate was continuously introduced into the 10-tier plate column having a column diameter of 0.3 m, at its uppermost tier at a feed rate of 52 kg/hr, while water vapor was jetted thereinto at the lowermost tier of the column at a flow rate of 86 kg/hr, so that the EVOH solution was contacted with water vapor in countercurrent flow in the column. The temperature in the column was 130°C, and the pressure therein was 3 kg/cm<sup>2</sup>. The methanol vapor and water vapor led out of the column through its top was condensed in the condenser, and the resulting aqueous methanol solution was recovered. The aqueous EVOH composition thus produced was continuously taken out of the column through its bottom. This contained 0.04 parts by weight of methanol, 105 parts by weight of water and 1.5 parts by weight, in terms of sodium, of sodium acetate, relative to 100 parts by weight of EVOH therein.

[0114]

Next, the aqueous EVOH composition was fed into the twin-screw extruder shown in Fig. 4. Its feed rate was 50 kg/hr



(containing water). On the other hand, an aqueous acetic acid solution (0.5 g/liter) was fed into the extruder through the wash supply unit 37 at a feedrate of 600 liters/hr; and an aqueous treating solution comprising acetic acid/boric acid/sodium acetate/magnesium acetate/potassium dihydrogenphosphate was fed thereinto through the minor component supply unit 39. The feedrate of the treating solution was 2.4 liters/hr. Precisely, the treating solution contained 5.0 g/liter of acetic acid, 15 g/liter of boric acid, 4.6 g/liter of sodium acetate, 3.0 g/liter of magnesium acetate tetrahydrate and 1.4 g/liter of potassium dihydrogenphosphate. The details of the twin-screw extruder used herein are mentioned below.

Type: twin-screw extruder,

L/D: 45.5,

Diameter: 47 mm $\phi$ ,

Screw: uniaxial full engaging type,

Screw revolution: 450 rpm,

Cylinder temperature: 95°C,

Die temperature: 120°C,

Number of die holes: 5 (3 mm $\phi$ ).

[0115]

The constitution of the twin-screw extruder is shown in detail in Fig. 4. The extruder comprises a raw material supply unit 36, a wash supply unit 37, a dewatering unit 38, and a minor component supply unit 39, and the dewatering unit is equipped

with a wedge wire-type dewatering slits 41. For the screws, a full-flight screw 42 is combined with a reverse-flight screw 43 as illustrated, and a seal ring 44 is fitted thereto. At the tip of the cylinder, disposed is a temperature sensor 40.

[0116]

The EVOH resin melt thus processed in the extruder was cut with the hot cutter into pellets (C'). Thus extruded and cut, the water content of the EVOH resin pellets was 23 % by weight. The thus-obtained pellets were dried in the fluidized drier at 90°C for 15 hours, and then in the ventilation drier at 105°C for 15 hours. Their water content reduced to 0.1 % by weight. After thus dried, the acetic acid content of the EVOH resin pellets (D') was 320 ppm, the boron compound content thereof was 270 ppm in terms of boron, and the phosphoric acid compound content thereof was 100 ppm in terms of phosphate radical. Regarding the alkali metal salt content of the pellets, the potassium salt content thereof was 38 ppm in terms of metal, and the sodium salt content thereof was 170 ppm in terms of metal. Regarding the alkaline earth metal content of the pellets, the magnesium salt content thereof was 40 ppm in terms of metal. MI of the pellets was 1.7 g/10 min.

[0117]

The dry pellets (D') were formed into a single-layer film. While they were in the extruder for single-layer film formation, the motor torque and the torque change were measured. The motor

torque for film extrusion was 205 kg·cm; and the torque change was 25 kg·cm.

[0118]

Comparative Example 1:

An EVOH solution containing 100 parts by weight of EVOH having an ethylene content of 32 mol% and a degree of saponification of 99.5 mol%, 100 parts by weight of methanol, 50 parts by weight of water and 2 parts by weight, in terms of sodium, of sodium acetate was extruded through the circular hole of a metal plate into a coagulating bath of aqueous 10 % methanol solution, and coagulated to be strands, which were then cut with a strand cutter into pellets having a diameter of about 3 mm and a length of about 5 mm. Methanol evaporated from the coagulating bath, and the methanol concentration around the bath was 180 ppm. This worsened the environment in the working area.

[0119]

The pellets obtained herein were fed into the same column vessel having a diameter of 0.8 m and a height of 4 m as in Example 1, through its top at a feed rate of 33 kg/hr (containing the aqueous methanol solution), while an aqueous acetic acid solution (0.5 g/liter, 50°C) was fed thereinto through its lower part at a feed rate of 500 liters/hr, and the washed pellets were continuously taken out of the processor through its bottom. In this process, the pellets were difficult to smoothly take out, as they much fused, and the line was difficult to continuously

drive. The water content of the pellets obtained herein was 55 %; and the sodium acetate content thereof was 0.008 % by weight in terms of sodium.

[0120]

3.5 kg of the EVOH resin pellets (having a water content of 55 % by weight) obtained herein were dipped in 6 liters of an aqueous solution containing 0.4 g/liter of acetic acid, 0.4 g/liter of sodium acetate, 0.3 g/liter of magnesium acetate, 0.1 g/liter of potassium dihydrogenphosphate and 0.7 g/liter of boric acid, at 25°C for 6 hours. After thus dipped, they were dewatered, and the resulting EVOH resin pellets (having a water content of 55 % by weight) was dried in a fluidized drier at 80°C for 15 hours and then in a ventilation drier at 100°C for 24 hours. The dried pellets had a water content of 0.3 %.

[0121]

The acetic acid content of the dried EVOH resin pellets was 300 ppm; the boron compound content thereof was 270 ppm in terms of boron; and the phosphoric acid compound content thereof was 100 ppm in terms of phosphate radical. Regarding the alkali metal salt contents of the pellets, the potassium salt content thereof was 40 ppm in terms of metal, and the sodium salt content thereof was 130 ppm in terms of metal. Regarding the alkaline earth metal content of the pellets, the magnesium salt content thereof was 36 ppm in terms of metal. MI of the pellets was 1.5 g/10 min.

[0122]

The dry pellets were formed into a single-layer film. While they were in the extruder for single-layer film formation, the motor torque and the torque change were measured. The motor torque for film extrusion was 1000 kg·cm or more; and the torque change was 300 kg·cm or more. Stable extrusion of the pellets for film formation was impossible.

[0123]

[Advantages of the Invention]

The present invention provides a method for producing an EVOH resin that ensures efficient removal of alcohol not worsening the environment in and around working areas. It also provides a method for producing pellets of the EVOH resin, of which the advantage is that it enables stable production and rapid washing of the pellets.

The EVOH resin pellets thus produced can be fed smoothly into extruders, enjoying stable extrusion and thermal stability in long-run extrusion working lines.

[Brief Description of the Drawings]

[Fig. 1]

A schematic view showing one example of the constitution of a hot cutter used in the invention

[Fig. 2]

An outline view showing the process of Example 1

**[Fig. 3]**

Aschematic view showing the constitution of the twin-screw extruder used in Example 1

**[Fig. 4]**

Aschematic view showing the constitution of the twin-screw extruder used in Example 3

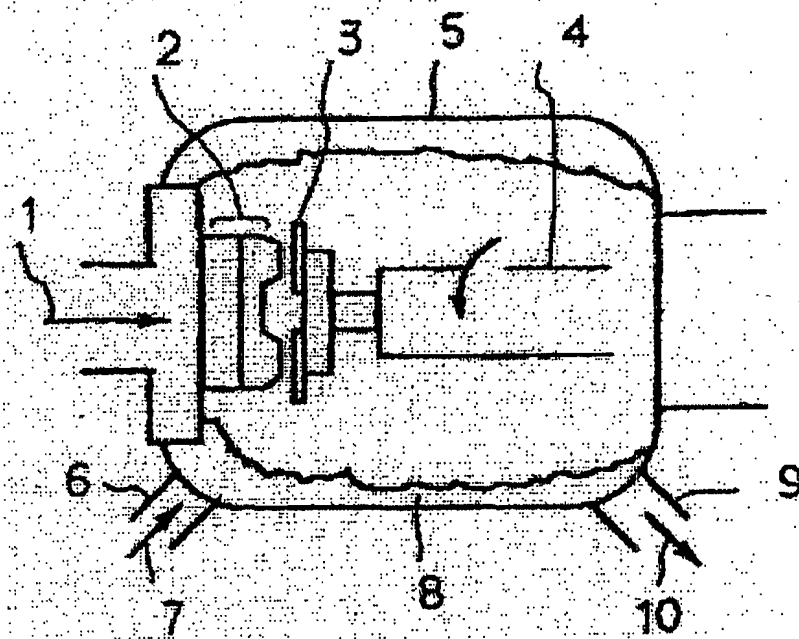
**[Explanations of Letters or Numerals]**

- 1: Aqueous EVOH composition inlet port
- 2: Die
- 3: Rotary blade
- 4: Rotation axis
- 5: Cutter box
- 6: Cooling water inlet port
- 7: Cooling water
- 8: Water membrane
- 9: Pellets take-out port
- 10: Cooling water and pellets
- 11: Plate column
- 12: Condenser
- 13: Kneader
- 14, 17: Hot cutter
- 15: Column vessel
- 16: Twin-screw extruder
- 18: Fluidized drier
- 19: Ventilation drier

- 20: Water vapor supply duct
- 21: EVOH solution supply duct
- 22: Vapor discharge duct
- 23: Aqueous composition take-out duct
- 24: Pellet supply duct
- 25: Solution discharge duct
- 26: Solution supply duct
- 27: Pellet take-out duct
- 28: Liquid discharge port in kneader
- 29: Raw material supply unit
- 30: Dewatering unit
- 31: Minor component supply unit
- 32: Temperature sensor
- 33: Dewatering slit
- 34: Full-flight screw
- 35: Reverse-flight screw
- 36: Raw material supply unit
- 37: Wash supply unit
- 38: Dewatering unit
- 39: Minor component supply unit
- 40: Temperature sensor
- 41: Dewatering slit
- 42: Full-flight screw
- 43: Reverse-flight screw
- 44: Seal ring

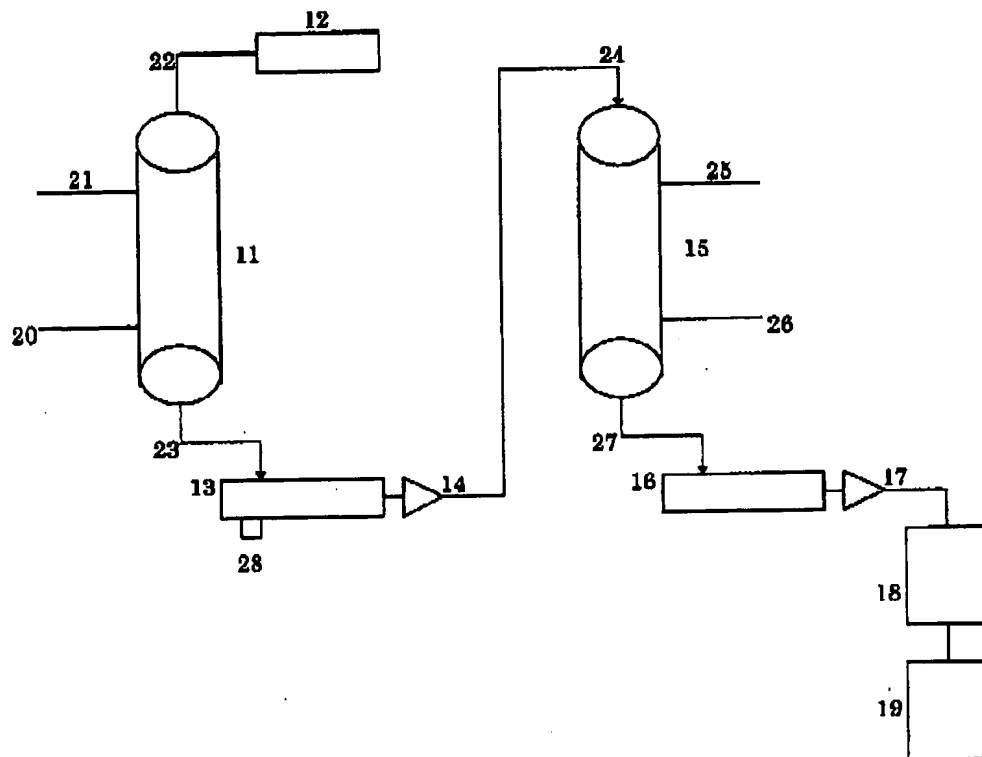
[Designation of Document] Drawings

[Fig. 1]

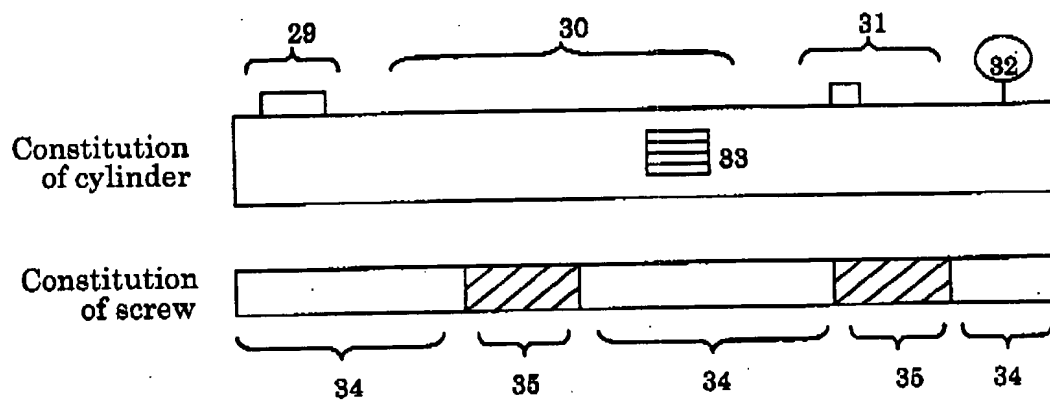




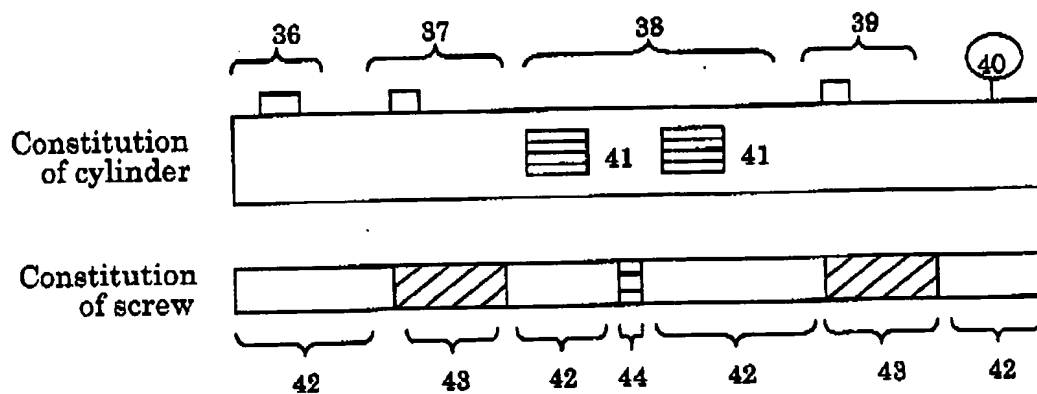
[Fig. 2]



[Fig. 3]



[Fig. 4]



[Designation of Document]      Abstract

[Abstract]

[Problem] Provided is a method for producing an ethylene-vinyl alcohol copolymer resin that ensures efficient removal of alcohol not worsening the environment in and around working areas. Also provided is a method for producing pellets of the ethylene-vinyl alcohol copolymer resin, of which the advantages are that the method enables stable production and rapid washing of the pellets and that the pellets produced can be fed smoothly into extruders, enjoying stable extrusion and thermal stability in long-run extrusion working lines.

[Means for Resolution] The method comprises a step of introducing an ethylene-vinyl alcohol copolymer solution that contains at least 50 parts by weight, relative to 100 parts by weight of the ethylene-vinyl alcohol copolymer therein, of an alcohol having a boiling point of not higher than 100°C, into an apparatus, and contacting it with water in the apparatus, thereby letting the alcohol out along with water and taking the resulting aqueous ethylene-vinyl alcohol copolymer composition that contains from 0 to 10 parts by weight of the alcohol and from 10 to 1000 parts by weight of water, relative to 100 parts by weight of the ethylene-vinyl alcohol copolymer therein, out of the apparatus (step 1), and a step of feeding the aqueous ethylene-vinyl alcohol copolymer composition into an extruder, kneading it in melt therein, and then extruding the copolymer

out of the extruder (step 2). And the method comprises cutting the ethylene-vinyl alcohol copolymer resin extruded out of the extruder in the step 2 in the resin production method.

[Drawing Selected] None.

**Applicant's History Information**

Identification Number [000001085]

1. Date of Change: August 9, 1990

[Reason of Change] New Registration

[Address] 1621, Sakazu, Kurashiki-City,  
Okayama-Pref.

[Name] Kuraray Co., Ltd.

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**